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Magnetic Rotatory Power of Crystalline Nickel Sulphate in the Short Infra-Red Spectrum

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The magneto-optical activity of thin crystals of nickel sulphate α-hexahydrate has been measured by means of the spectroradiometric method in the spectral range 0.7μ to 1.9μ and for ordinary and low ($-125°C$) temperatures. The curves showing the dispersion of the rotation have marked anomalies in the region of $\lambda\ 0.69\mu$ and particularly 1.16μ, matching the ones found in the optical rotation for these wave-lengths. The ratio of the rotations at low temperatures and room temperature is itself an anomalous curve. The effects can be qualitatively explained on the basis of the inverse Zeeman effect.

THE interesting anomalous optical properties of thin crystals of nickel sulphate α-hexahydrate have been studied at some length, particularly as regards optical activity, circular dichroism, and absorption in the wave-length range 0.25μ–2.3μ at ordinary[1] and low[2] temperatures. The magnetic rotation has also been measured in the visible[3] and ultraviolet[4] regions. The present work is a study of the magnetic rotatory power (Faraday rotation) in the short infra-red, particularly in the region of the absorption band at $\lambda\ 1.16\mu$, where the optical activity shows such a striking anomaly. This has been done for both ordinary and low temperatures.

EXPERIMENTAL METHODS

The spectroradiometric method of measuring magnetic rotatory dispersion has been described[5] several times and need be only briefly mentioned. Light from a special tungsten strip filament lamp was concentrated by a spherical aluminized glass mirror into a narrow conical beam, polarized by passage through a double-image prism (only one image being used) with principal plane at 45° azimuth. This light traversed the conically bored polepieces of a large electromagnet, converging to a focus on the crystal specimen between the poles. It was then in turn focused by a second concave mirror, after passage through a large Wollaston calcite double-image prism (whose principal planes were vertical and horizontal) on the double slit of the spectrometer. The two slits were vertically above one another, and one of the two images from the Wollaston fell on each slit. After passage through the spectrometer, which used a 9-cm high heavy glass 45° prism with Wadsworth mirror mounting and two concave mirrors of 40-cm focus, the two beams fell on the two arms of a vacuum differential thermopile which was connected with a Kipp and Sons ZC galvanometer. When the system was balanced (i.e., the two beams of equal intensity), with no magnetic field, the galvanometer spot stood at zero, but exciting the magnet, with the crystal between the polepieces, caused a small Faraday rotation of the plane of polarization of the beam which fell on the Wollaston prism and the resulting unbalance gave a galvanometer deflection. To interpret this deflection in degrees or minutes of rotation, it was compared with that produced by the mechanical rotation of the polarizer through 1°. Measurements could be made in general for wave-lengths between 0.5μ and 2.3μ although the results in the present case are confined to the region 0.7μ–1.9μ.

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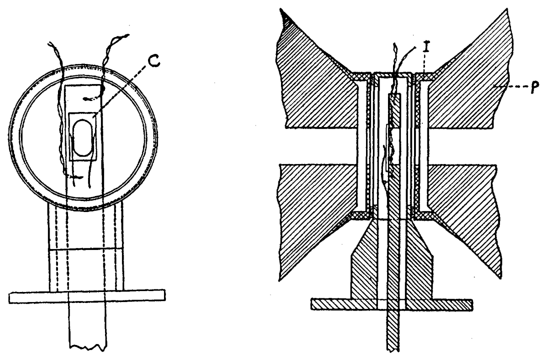

FIG. 1. Crystal holder and method of cooling. *C*, crystal; *P*, magnet polepieces; *I*, Inconel caps.

The method of keeping the crystal specimen at a suitable low temperature requires a little description. Preliminary experiments involving various ways of cooling the crystal by more or less intimate contact with liquid air in general proved unsuccessful, the chief difficulty encountered being the film of condensed moisture on the specimen or windows or both. The problem was finally solved by mounting the crystal (Fig. 1) on a flat brass bar, the end of which extended into a flask of liquid air and past which was flowing a stream of cold evaporated air. To avoid the disturbing effect due to the proximity of the relatively warm polepieces, these were sheathed with specially designed Inconel caps. The resulting temperature, which was measured by two small calibrated thermocouples in contact with the bar just above and below the crystal, could be maintained very steady at −125°C, and this was quite satisfactory for our purpose. The room temperature measurements were made at 25°C. Suitable water-cooling arrangements for the magnet helped in keeping this, as well as the lower temperature, satisfactorily constant.

All rotation measurements were made for a field of approximately 13,300 oersteds which was used throughout the experiments. The rotations were determined for reversal of this field in terms of the galvanometer deflections produced, as already described.

The cleaved crystal laminae varied in thickness from 0.4 to 0.9 mm; some eight different specimens were used altogether. Their diameter was only slightly larger than the 5-mm diaphragm hole over which they were mounted. The optic axis was, of course, perpendicular to the crystal surface. Both right and left crystals were used. Since it might conceivably be urged that the anomaly found in the magnetic rotation was a spurious effect connected with the great anomaly in the optical rotation[6] at λ 1.16μ, some measurements were made on a combination of the two sorts of crystals which gave a net *optical* rotation of almost zero. All results on right- and left-hand crystals and on the combination gave magnetic rotations of the same sign and essentially the same magnitude.

RESULTS AND DISCUSSION

The results are shown in Figs. 2 and 3. Too much reliance should not be placed on the absolute values of the ordinates as almost the entire emphasis in this work was on the relative values, i.e., the *dispersion* of the rotation (i.e., of the Verdet constant), or *form* of the curves. A striking anomaly, somewhat resembling that found for the optical rotation[6] at λ 1.16μ, is seen to hold also for the magnetic rotation. (There is also a minor anomaly undoubtedly connected with the absorption band at 0.69μ.) There is this important difference, however, that while in the natural or optical rotation the temperature effect is almost independent of wave-length,[7] in the present case the *ratio* of the two rotations is itself an "anomalous" function of the wave-length, as shown in Fig. 3.

In attempting to explain these results we at once find ourselves in difficulty because of a lack of knowledge of the refractive index, or rather indices, of this material in this spectral region. As a matter of fact we have already expended a great deal of effort in trying to clear up this matter but the results to date are not such as will justify their use. It will apparently be necessary to attack the problem from another angle.

In the meantime, however, a fairly satisfactory qualitative explanation can be offered for the form of the curves of Figs. 2 and 3. If the explanation of the Faraday rotation is based on the inverse Zeëman effect and if it is further assumed that the intensities of the absorption bands are unequal, an anomaly[8] of the type of

[6] See reference 1, Ingersoll, Rudnick, Slack, and Underwood, p. 1149.
[7] See reference 2, Rudnick and Ingersoll, p. 624.
[8] See Wilhelm Schütz, Wien-Harms Handbuch **16**, 82 (1936).

Fig. 2 results. To see if it would be possible to explain, on a reasonable basis, the form of the ratio curve as given in Fig. 3, we used the general equation for magnetic rotation,[9] written for a single term in the summation as

$$\alpha = NHL\frac{(n^2+2)^2}{9n}\left[A\frac{\omega^2}{(\omega_0^2-\omega^2)^2} + B\frac{\omega^2}{\omega_0^2-\omega^2} + \frac{C}{T}\frac{\omega^2}{\omega_0^2-\omega^2}\right], \quad (1)$$

ω being the frequency of the light.

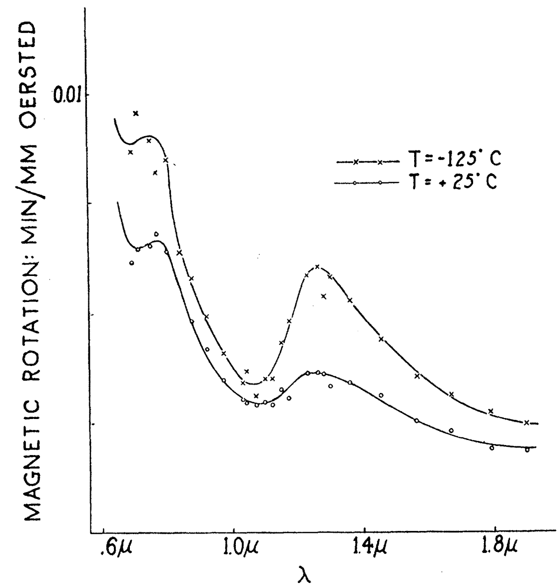

FIG. 2. Dispersion of the magnetic rotation of crystalline nickel sulphate at room temperature and low temperature.

[9] Reference 8, p. 86.

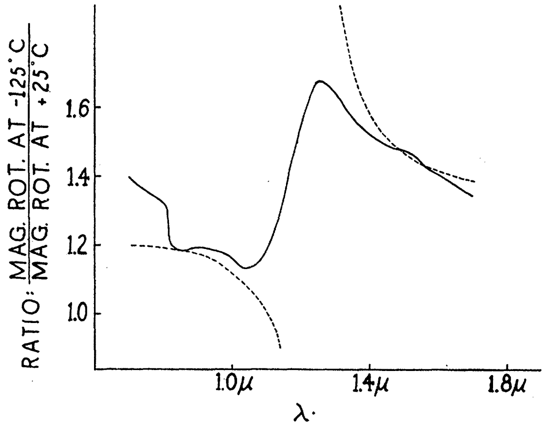

FIG. 3. Solid line, observed ratio of the magnetic rotations of crystalline nickel sulphate at −125°C and 25°C. Dotted line, theoretical ratio calculated from Eq. (1).

Lacking more exact information on the variation of n, the terms preceding the bracket have been treated as constant. We then find that if we assume $B/A = -0.01$ and $C/A = -5.00$ and if we furthermore apply an over-all factor of about $\frac{3}{4}$, there results a curve (see dotted line in Fig. 3) which has some qualitative resemblance to the one found by experiment. This is perhaps as far as it is profitable to go until more can be learned about the dispersion of the refractive index.

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